AEOLIAN DELIVERY OF ORGANIC MATTER TO A MIDDLE PERMIAN DEEPWATER RAMP

A Thesis

by

SINEM ARTAN

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2011

Major Subject: Geology

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Approved by:

Co-Chairs of Committee,	Bruce Herbert
	Mike Tice
Committee Member,	Thomas McDonald
Head of Department,	Andreas Kronenberg

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ABSTRACT

Aeolian Delivery of Organic Matter to a Middle Permian Deepwater Ramp.

(May 2011)

Sinem Artan, B.S., Ankara University

Chair of Advisory Committee: Dr. Bruce Herbert

Windblown dust is a significant source of sediment and organic matter for many basins, but its influence on ancient basins can be difficult to detect and quantify. We quantified the biomarker content, including *n*-alkanes, hopanes, and steranes of the Brushy Canyon Formation sandstones and siltstones to evaluate the significance of windblown dust in delivery of sediment and terrestrial organic matter to the Middle Permian Delaware Basin. Ramp siltstones of the basin have been interpreted as representing deposits of unconfined low-density turbidity currents or "aeolo-marine" sediments.

We analyzed the organic contents of five samples of channel-confined turbiditic sandstones and siltstones and five samples of ramp siltstones outcropping in the Guadalupe Mountains National Park, West Texas, to estimate the relative proportions of terrestrial and marine organic matter in the two types of host rocks. The total organic carbon content of all samples varied from 0.07% - 2.04%. The abundance of high molecular weight *n*-alkanes (*n*-C27 and greater) suggests that terrestrial organic matter was present in nearly all samples. Terrestrial organic matter input to the basin was

characterized using a crossplot of pristane/*n*-C_{17} versus phytane/*n*-C_{18}. Ramp siltstones showed ~10-fold greater variation in terrestrial content than did turbiditic sandstones and siltstones. This observation is more consistent with the aeolo-marine interpretation of ramp siltstones, and suggests that terrestrial organic matter was delivered to the Delaware Basin by wind transport during deposition of the Brushy Canyon Formation.

To my mother, Semra Artan, and my father, Mehmet Ali Artan

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my co-advisors, Dr. Bruce Herbert and Dr. Mike Tice, for their time, guidance and advice throughout the course of this research. I also wish to thank the member of my graduate committee, Dr. Thomas McDonald, for endless analytical support, technical advice and patience.

I would particularly thank Dr. Mike Tice for providing the samples used in this study and for his generous help and support.

The completion of this study would not have been possible without the support of my sponsoring company, Turkish Petroleum Corporation (TPAO). I would like to thank them for their encouragement and financial support.

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CHAPTER I

INTRODUCTION

Deep-water sandy marine sediments have been the subject of considerable research over the past two decades in both academic study and industrial interest. The exploration and production industries are focusing on turbidites because these deposits, in otherwise low porosity/permeability sequences, represent significant potential oil and gas reservoirs (Fetter et al., 2009). Siliciclastic turbidites also represent huge volumes of sediments, which play an important role in understanding sediment transport mechanisms from coastal to deep sea areas. Turbidity currents, which carry siliciclastic material (particularly grains greater than clay-sized) from shallow to deep-water basins, also transfer organic matter from both shallow marine and terrestrial environments (Sullwold, 1961). Alternatively, aeolian transport has been considered as another significant process for the organic matter input to marine sedimentary environments (Simoneit and Eglinton, 1977).

Organic matter deposition is an important factor that affects the amount of organic matter stored in sediments (Hyne, 1978). There are a wide range of processes that transport organic matter to basins including physical, geochemical and biological processes. Allochthonous (terrigenous) material is transported by rivers or wind to

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This thesis follows the style of Organic Geochemistry.

marine systems whereas autochthonous (marine) organic matter is produced in the surface water and sinks through the water column. Turbidity currents provide an additional organic matter transport mechanism to depositional basins. However, because turbidite emplacement is discontinuous, it produces a heterogeneous distribution of organic matter type, quantity and diagenesis in sediments (Cowie et al., 1995; Meyers et al., 1996). On the other hand, it is challenging to determine land-derived organic matter inputs at open ocean regions; however, terrestrial organic matter has a remarkable geochemical importance (Peltzer and Gagosian, 1989) because their delivery rate is considered as significant as of marine-derived organic matter to the seafloor (Zafiriou et al., 1985).

The character of organic mater in deep-water sediments is controlled by many factors, such as its source, transport mechanisms and depositional environment conditions (Meyers and Silliman, 1996). Because the amount of organic matter and its characteristics are influenced by various processes, much information could be inferred from the organic matter content of sedimentary rocks. A number of proxies, such as isotopic ratios and trace elements, have been used to asses the paleodepositional environment, source and thermal maturity of sediments in basins (Hedges et al., 1997). Biomarkers are one of these important approaches, which are useful in sedimentary rocks due to their well preserved basic chemical structures through processes associated with sedimentation and diagenesis (Peters and Moldowan, 1993).

In the present study, organic geochemical characterization was conducted with a set of samples from deep-water ramp sedimentary rocks using biological markers (or

chemical fossils) in order to test hypotheses concerning aeolian inputs of terrestrial organic matter in the Middle Permian Brushy Canyon Formation. Turbiditic siliciclastic deposits of the study area were situated in the Delaware Basin, west Texas and southeast New Mexico (Beaubouef et al., 1999). The Brushy Canyon Formation mainly comprises deep-water ramp siltstones and channel-confined sandstones in the basin (King 1948; Beaubouef et al., 1999). Comparing organic matter content in these deep-water sedimentary rocks from different facies of the Brushy Canyon Formation provides us an opportunity to detect the significance of windblown dust's influence in the basin. Different interpretations in recent studies (Beaubouef et al., 1999; Gardner and Sonnenfeld, 1996; Fischer and Sarnthein, 1987) regarding the deposition and transport mechanisms of ramp siltstones also directed this research to focus on the presence of aeoilan delivery of terrestrial organic matter in the basin.

BIOMARKER IMPORTANCE

Biomarkers are individual organic compounds of sedimentary rocks and oils which are derived from biological precursors. They are considered to be both those found in living organisms and those found in sediments. In this thesis, biomarkers particularly refer to molecular fossils, derived from biochemicals, mainly hydrocarbons. The chemical structure of hydrocarbons can be preserved through depositional and diagenetic processes whereas the morphology of particles is frequently not preserved (Brocks and Summons 2004; Peters et al., 2005). In marine sediments, characterization

of biomarkers provides diagnostic information of the biological origin of sedimentary organic matter; the environmental conditions during its deposition and diagenesis, thermal maturity and geological age with broad constraints (Peters et al., 2005).

Various biomarker and non-biomarker parameters can be applied to the interpretation and evaluation of deep-water marine sedimentary environments. Several biological marker compounds found in sediments have been used to assess organic matter source and chemical depositional environment where it is deposited. For instance, the C_{35} homohopane index can be used to assess the degree of oxicity under which marine sediments were deposited (Peters et al., 2005). In addition, specific patterns of n-alkane distributions and their ratio to isoprenoids have been examined to evaluate the source of organic matter in sedimentary rocks. Moreover, biomarkers also undergo some systematic transformations during diagenesis, and these changes in their compositions can therefore be used to measure thermal maturity level of sedimentary rocks (Pratt et al., 1992).

RESEARCH OBJECTIVES

The primary objective of the study is to compare the organic matter content of the sedimentary rocks from the Middle Permian Brushy Canyon Formation in order to test hypotheses for the origin of organic matter in ramp siltstones. Sedimentary organic matter is produced by a variety of biological and thermal processes. Therefore, understanding thermal maturity, oxicity and the organic matter source is significant.

This research will quantify the organic biological compounds, including *n*-alkanes, isoprenoids, hopanes and steranes using gas chromatography/flame ionization detection (GC/FID) and gas chromatography/mass spectrometry (GC/MS). Within this sense, the specific objectives are the following:

1- To document *n*-alkane distribution and isoprenoids of each rock sample from the different facies of the Brushy Canyon Formation in order to identify sources of organic material.

2- To quantify biomarker parameters, including sterane (m/z 217, 231) and hopane (m/z 191) ratios, and interpret oxicity of the paleodepositional environment and maturity levels.

CHAPTER II

AEOLIAN DELIVERY OF ORGANIC MATTER TO A MIDDLE PERMIAN DEEPWATER RAMP

Windblown dust is a significant source of sediment (Rea, 1994; Kocurek and Lancaster, 1999; Simpson et al., 2008) and organic matter (Simoneit and Eglinton, 1977) for many modern basins. Deep-water sediments dominated by aeolian dust, which is carried by dust storms originating in the arid and semi-arid areas of the continents, have drawn the attention of geologists since late 1950s. The amount of sediment delivered to the ocean by wind flux is estimated to be about 0.1-0.2 x 10^{15} t yr^{-1}, which is approximately 1% of the total river input of 15-20 x 10^{15} t yr^{-1} (Rea, 1994; Rea, 2009). Despite the fact that the data base for the organic carbon supplied by wind is very weak, aeolian inputs of terrestrial organic matter to the surface ocean is estimated to be as large as 0.1-0.3Gt yr^{-1} (Romankevich 1984; Zafiriou et al., 1985; Hedges et al., 1997).

The identification of windblown dust particles in marine sediments was initially made by Radczewski (1939). He indicates the presence of iron stained quartz particles as evidence of windblown material derived from terrestrial origin. According to Simoneit (1977), the actual input of aeolian dust to marine sediments occurs by two major pathways: dry fallout and wet washout. Once the dust falls out or gets washed out by rain onto the sea surface, it rapidly aggregates into small lumps (Kranck, 1973). This floc formation appears to be aided by the presence of organic matter (Gordon, 1970).

The fallout of dust produces silty and sandy beds and feeds shallow water sand wedges. Then turbidity currents move sand to deep water and allow deposition in channels (Sarnthein and Diester-Haas, 1977; Fischer and Sarnthein, 1988).

Terrestrial organic matter contribution in marine sediments is usually documented by analyzing stable isotopic compositions and C/N ratio of bulk organic mixtures. Additionally, molecular compounds, namely biomarkers, have been used as an alternative approach to characterize sedimentary organic matter (Hedges et al., 1997 and references therein). For instance, long chain *n*-alkanes with an odd over even carbon predominance are mostly found in terrestrial components in marine sediments which are derived from higher land plants (Eglinton and Hamilton, 1967). Fine-grained sediments, which can be easily transported by winds from lands, contain most of the hydrocarbon component of atmospheric dusts (Van Vaeck and Van Cauwenburghe, 1978). These components include the biomarker compounds which are diagnostic for identification of organic matter sources.

However, the influence of windblown dust on ancient basins can be difficult to detect and quantify. Sandstones and siltstones of the Middle Permian Brushy Canyon Formation in west Texas and southeast New Mexico were deposited in the Delaware Basin during a third-order relative sea level highstand (King, 1948; Harms, 1974; Gardner and Sonnenfeld, 1996; Sageman et al., 1998; Beaubouef et al., 1999) (Figure 1). Sandstones cropping out in large (tens of meters thick and kilometers long) channel forms in the Guadalupe Mountains National Park are now generally accepted as turbidites (Fischer and Sarnthein, 1988; Beaubouef et al., 1999; Gardner and Borer,

2000; Gardner and Sonnenfeld, 1996). Out-of-channel finely laminated siltstones have been interpreted as either the deposits of unconfined, low density, slowly moving turbidity currents (Beaubouef et al., 1999; Gardner and Sonnenfeld, 1996) or as pelagic silts transported to the basin by wind ("aeolo-marine deposits" of Fischer and Sarnthein, 1988). The specific objective of this study is to compare the organic matter preserved in these ramp siltstones and turbiditic sandstones in order to test hypotheses for the origin of these deposits. Specifically, we quantified the biomarker content of the Brushy Canyon Formation sandstones and siltstones to recognize the source of organic matter, assess the oxicity of depositional environment; and the thermal maturity.

GEOLOGICAL BACKGROUND

The Brushy Canyon Formation is the lowermost unit of the Guadalupian (271-260 Ma) Delaware Mountain Group and is about 300 m thick in the western Permian Basin, west Texas. The formation is bounded above by Cherry Canyon Sandstone Tongue and below by the Cutoff shaly member of the Bone Spring Formation (King, 1948). It mainly consists of submarine canyon fill, slope and basin-floor deposits (Gardner and Sonnenfeld, 1996). The rocks in this study are from upper slope facies of the Brushy Canyon Formation, and consist of fine-grained sandstones and siltstones.

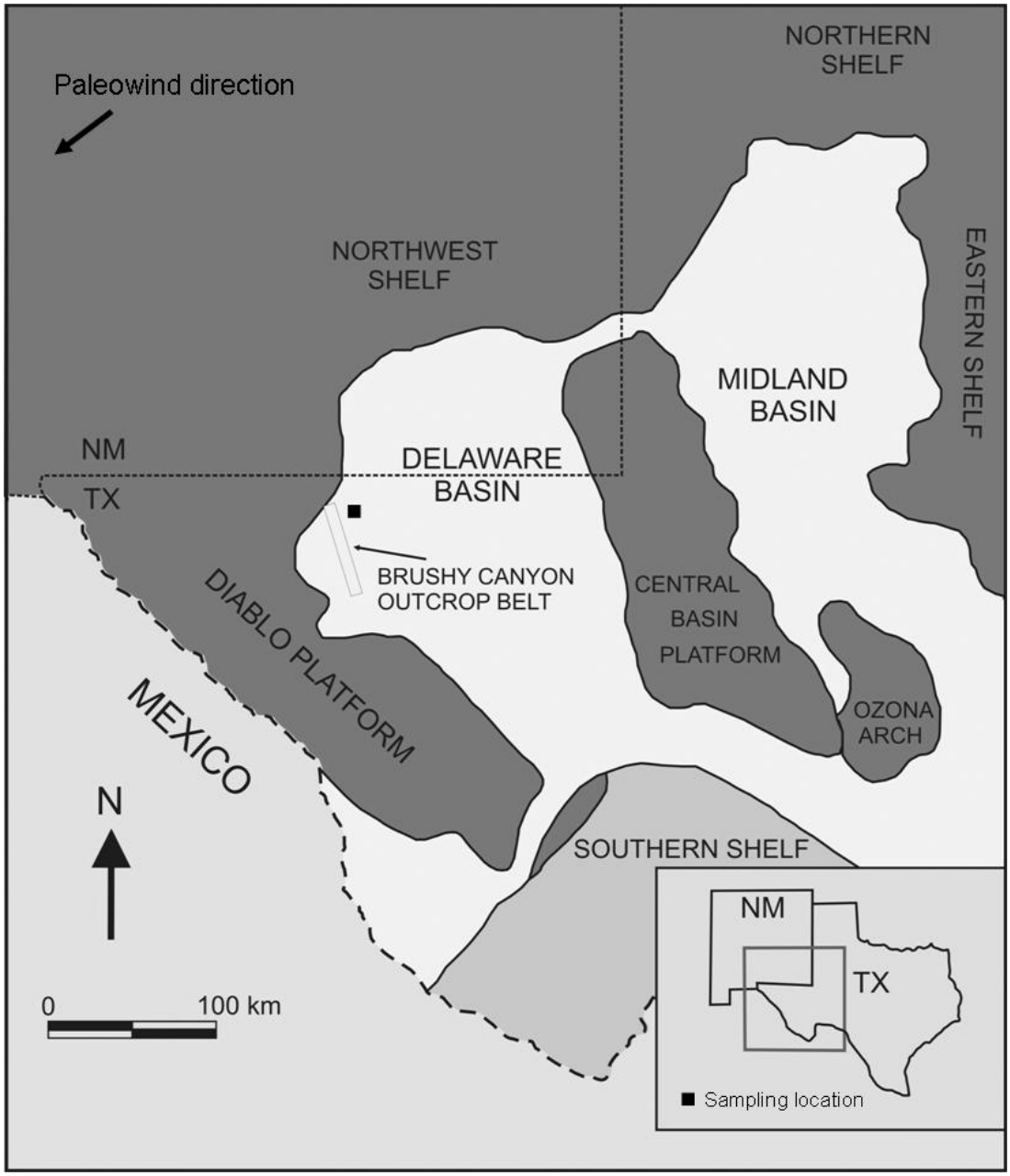

Figure 1. Geological setting of the Brushy Canyon Formation, early Guadalupian (Permian) (Modified after Beaubouef et al., 1999). Map includes paleowind direction (Parrish and Peterson, 1988; Sageman et al., 1998).

During the middle Permian, siliciclastic sediments were deposited as submarine complexes in the basin, and the uppermost siltstones of the Brushy Canyon Formation were cut by channels (King, 1948). Slope sediments of the upper Brushy Canyon Formation are primarily composed of three facies: (1) thinly bedded sandstones interpreted as Bouma C and D divisions (Beabouef et al., 1999; Gardner and Sonnenfeld, 1996); (2) structureless sandstone, interpreted as Bouma A divisions (Beabouef et al., 1999; Gardner and Sonnenfeld, 1996); and (3) laminated siltstones, which forms the bulk of the Brushy Canyon Formation.

On the slope, turbiditic sandstones fill channel forms completely encompassed by thick laminated siltstones (Harms 1974; Sageman et al., 1998). Siltstones make up about 90% of the Brushy Canyon formation (Beaubouef et al., 1999) and contain 0.5%-3% organic carbon (Sageman at el., 1998). If they are aeolo-marine, then wind transport could have been a major source of organics to the Delaware basin.

MATERIALS AND METHODS

Sample Selection and Preparation

Samples of Brushy Canyon Formation sandstones and siltstones were collected from natural outcrops and roadcuts in and around the Guadalupe Mountains National Park, west Texas. These samples were supplemented by a core sample which originally comes from southeast New Mexico. Three (3) outcrop samples, from different divisions of turbidite top, which were formed by high density of turbidity currents, and two (2) road-cut samples, from thinly bedded sandstones, which were formed by low density turbidity currents, were used. Siltstone samples can be subdivided into two groups based on their tone in outcrop and their bulk organic content: black siltstones and light siltstones. Two (2) black siltstones and two (2) light siltstones were used. One (1) core sample of light siltstone in addition to outcrop samples was also analyzed (Table 1).

Before organic geochemical analyses, all outcrop samples were cleaned, and weathered surfaces were removed. The samples were then crushed to a fine powder using a mortar and pestle. Before processing of each sample, all equipment was cleaned with dichloromethane ($MeCl_2$) in order to prevent laboratory contamination and cross contamination. The following stages of the experimental process (except TOC measurement) were performed in B&B Laboratories, College Station, Texas.

Table 1. Characteristics of sandstones and siltstones from the upper slope of the Brushy Canyon Formation.

Samples	Facies	Lithology	Depositional Processes	Location
G1 G2	Thinly bedded sandstone	Thinly laminated or cross laminated; light and dark grey; very fine grained sandstone; partial Bouma sequences (C and D divisions)	Low-density turbidity currents	Mid-slope channels
G3 G4 *G5 G6 G7	Laminated siltstones	Ungraded; thinly laminated sandy; lighter and black (organic-rich) siltstones	Unconfined low-energy turbidity currents OR windblown dust	Slope
G8 G9 G10	Structureless sandstone	Massive to normally graded; light and dark grey, fine grained sandstone; partial Bouma sequences (A and D divisions)	High-density turbidity currents	Mid-slope channels

***** Core sample: Laminated siltstone (subsurface sample) procured from the basin floor.

Solvent Extraction

Organic constituents of the rock powders were extracted by using Accelerated Solvent Extraction (ASE). With each set of extraction, a known amount of each sample, 4-10g, was added to stainless steel cells. Filter papers were put into both bottom and top of samples in order to retain particles in the cells. Samples were extracted with dichloromethane ($MeCl_2$) at elevated temperature (100°C) and pressure (1500psi). Extracts were then transferred to graduated glass tubes, and then placed vertically in an

evaporator. The solvent was evaporated to approximately 10mL with a Turbo LV Evaporator, at 40 °C and 25psi. After solvent evaporation, the samples were placed into a 58 °C water bath, and were further concentrated to three milliliters. In order to calculate the amount of extractable organic matter (EOM) within a sample, a portion (100µl) of each sample extract was added onto pre-weighed adsorbent paper. The paper with extracted sample then was dried in a 40 °C oven for 2 minutes and was re-weighed. The numbers were noted as a weight (mg) of one hundred micro liter lipid/EOM weights for each sample. Final EOM (based on dry weights) values were calculated by using the following equation:

EOM= [(EOM Wt. (mg)) (Final Extract Vol. (ml) / (Smpl Dry Wt. (g)) (0.10 ml)] x 1000

After EOM analysis, the extracts were concentrated to one milliliter and analyzed using Gas Chromatography/Flame Ionization (GC/FID) and Gas Chromatography/Mass Spectrometry (GC/MS).

Gas Chromatography/ Flame Ionization Detection

The measured saturated hydrocarbons in this study include *n*-alkanes (normal or straight chained alkanes) ranging from *n*-C11 to *n*-C40, the iso-alkanes (branched alkanes) pristane and phytane. Gas Chromatography/Flame Ionization (GC/FID) was

performed using a Hewlett–Packard 5890 Series II GC equipped with a flame ionization detector. For analysis of the saturated hydrocarbons, a 30 m Restek Scientific RTX-1 column (0.25 mm i.d. and 0.25 μm film thickness) was used with helium as carrier gas, and a split/splitless injection port operated in split mode. The GC oven temperature was programmed from 60 °C (initial hold time: 2 minutes) to 180 °C (final hold time: 0 minutes) at 12 °C/min, then to 300 °C at 6 °C/min where it was held for 18 minutes. The injection port and detector temperatures were 300 °C. Data were acquired and processed using HP Chemstation software.

The analyte concentrations were calculated using the internal standard method. Prior to the analysis a five-point calibration curve was established to determine the response factors (RFs) used to calculate analyte concentrations for each sample. The internal standard compounds were 5α-androstane and n-hexadecane-d_{34}.

Gas Chromatography/ Mass Spectrometry

Gas Chromatography/Mass Spectrometry (GC/MS) was performed using an Agilent 7890 series gas chromatograph equipped with a 5975 mass selective detector (MSD) operated in selected ion monitoring mode (SIM). Hopanes and steranes were analyzed using an Agilent Technologies HP-5MS column (60 m, 0.25mm i.d. and 0.25 μm film thickness), and a split/splitless injection port operated in splitless mode. The following GC oven program was used: Initial temperature of 60 °C for 0 minutes, ramp at 7 °C a minute to a final temperature of 315 °C and hold isothermally for 22 minutes.

The injection port temperature was 300 °C and the detector temperature was 290 °C. For the analysis of biomarkers, compounds were identified through retention time. Hopane and sterane distributions were quantified by measuring peak areas in the m/z 191 and m/z 217, 231 chromatograms, respectively.

Total Organic Carbon Content

A portion of each sample was acidified with a combination of HCl and ferrous chloride ($FeCl_2$) to remove carbonates. Carbonate-free samples were dried and analyzed for total organic carbon (TOC) content using the methods of Nelson and Sommers (1982) at the Soil Characterization Laboratory, Texas A&M University.

RESULTS

Total Organic Carbon (TOC)

Organic carbon contents (C_{org}) of these samples ranged between 0.07 and 2.04 wt% (Table 2). While TOC levels are marginal (<1%) for hydrocarbon generation in most of the ramp sediments, percentage of TOC exceeds 1.50 % in dark and organic rich sandstones and siltstones. The lowest carbon contents were found in the light-colored turbiditic sandstones whereas the highest contents were found in black siltstones.

Table 2. Data of total organic carbon, CPI, and isoprenoid/n-alkane ratios of the slope sedimentary rocks in the Brushy Canyon Formation, Delaware Basin.

Sample ID		**TOC%**	**CPI**	**Pr/*n*-C_{17}**	**Ph/*n*-C_{18}**
Thinly bedded sandstone (Light)	**G1**	0.10	1.09	0.94	0.66
Thinly bedded sandstone (Dark)	**G2**	1.10	1.23	1.51	1.05
Laminated siltsone (Grey)	**G3**	0.13	1.38	1.00	0.83
Laminated siltstone (Grey)	**G4**	0.19	1.06	2.00	1.14
Laminated siltstone (Core)	**G5**	0.14	1.02	0.57	0.88
Laminated siltstone (Black silt)	**G6**	2.04	1.07	1.48	0.91
Laminated siltstone (Black silt)	**G7**	1.59	1.08	2.01	0.98
Structureless Sandstone (Lighter)	**G8**	0.07	nd	0.75	0.57
Structureless Sandstone (Dark)	**G9**	0.22	1.00	1.53	1.11
Structureless Sandstone (Light)	**G10**	0.28	1.20	1.38	1.07

TOC: Total organic carbon

CPI: Carbon Preference Index: ½ [(C_{25}+C_{27}+C_{29}+C_{31}) / (C_{24}+C_{26}+C_{28}+C_{30}) + (C_{25}+C_{27}+C_{29}+C_{31}) / (C_{26}+C_{28}+C_{30}+C_{32})]

Molecular Characteristics of the Sedimentary Rocks

Various geochemical ratios have been calculated to assess the source, maturity and depositional environment of organic matter within the ramp sandstones and siltstones of the upper Brushy Canyon Formation. To understand the source of the sedimentary organic matter, *n*-alkane distribution patterns and iso-prenoidal ratios (Pr/*n*-C_{17} and Ph/*n*-C_{18}) were identified. The C_{35}-homohopane index was also calculated in order to asses the conditions of depositional environment. The carbon preference index (CPI), the C_{29} sterane ratios (20S/ (20S+20R)), the C_{32} hopanes (22S/ (22S+22R)) and

the tri-aromatic sterane ratios (TAI/ (TAI+TAII)) were computed to evaluate the maturity of organic matter with respect to the oil generation window.

n-Alkanes and Isoprenoids

GC-FID analysis showed the presence of *n*-alkanes ranging from C_{10} through C_{40} in most of the studied samples from the upper Brushy Canyon Formation (Figure 2). *n*-Alkane abundances varied while the maximum concentrations were found in the dark-colored thinly bedded sandstone and black siltstone samples. Although all samples, except G5, are surface samples and a loss of *n*-alkanes because of water washing and microbial activity is indicated by relatively low amounts of short chain *n*-alkanes (C_{10}-C_{16}), several trends can be seen. Odd-over-even predominance can be quantified by the carbon preference index (CPI). The CPI is defined as the ratio of odd *n*-alkanes to even *n*-alkanes between *n*-C_{24} and *n*-C_{32} and calculated by the equation (Bray and Evans, 1961): $\frac{1}{2}\{[(C_{25}+ C_{27}+C_{29}+C_{31})/(C_{24}+ C_{26}+C_{28}+C_{30})] + [(C_{25}+ C_{27}+C_{29}+C_{31})/(C_{26}+ C_{28}+C_{30}+C_{32})]\}$. Most of the *n*-alkane distributions in the studied samples had slightly elevated CPIs ranging from 1.00 to 1.38 (Table 2).

There are no systematic facies-related variations in *n*-alkane distributions. However, some samples of turbiditic sandstones (G1, G8) and laminated siltstones (G5, G6) showed relatively high concentration of short chain and mid-chain *n*-alkanes with no or slight odd over even predominance (CPI: 1.02 -1.09). The other samples (G2, G3, G4, G7, G9, G10) were primarily dominated by mid-chain and long-chain *n*-alkanes. Remarkable abundances of long-chain *n*-alkanes in some samples of laminated siltstones (G3 and G4) were also observed in comparison to the other samples. Although G3 is also dominated by short-chain *n*-alkanes, it exhibits high relative amounts of C_{27}, C_{29} and C_{33} *n*-alkanes with the highest odd over even predominance (CPI: 1.38) among all analyzed samples.

The identified isoprenoids, pristane (Pr) and phytane (Ph), are present in all samples. Pr/*n*-C_{17} and Ph/*n*-C_{18} ratios range from 0.75 to 2.01 and 0.57 to 1.14, respectively (Table 2).

Hopanes

The terpane mass chromatograms in Figure 3 for the ramp sandstone and siltstone samples of the Brushy Canyon Formation show the hopane distributions, which were determined by monitoring m/z 191. Peak identification is summarized in Table 3. In this study, the ratio of hopane isomers was used to estimate the depositional environment and maturity of the organic matter in sedimentary rocks. The C_{30} regular hopane is the most predominant peak followed by C_{29} norhopane in all the samples.

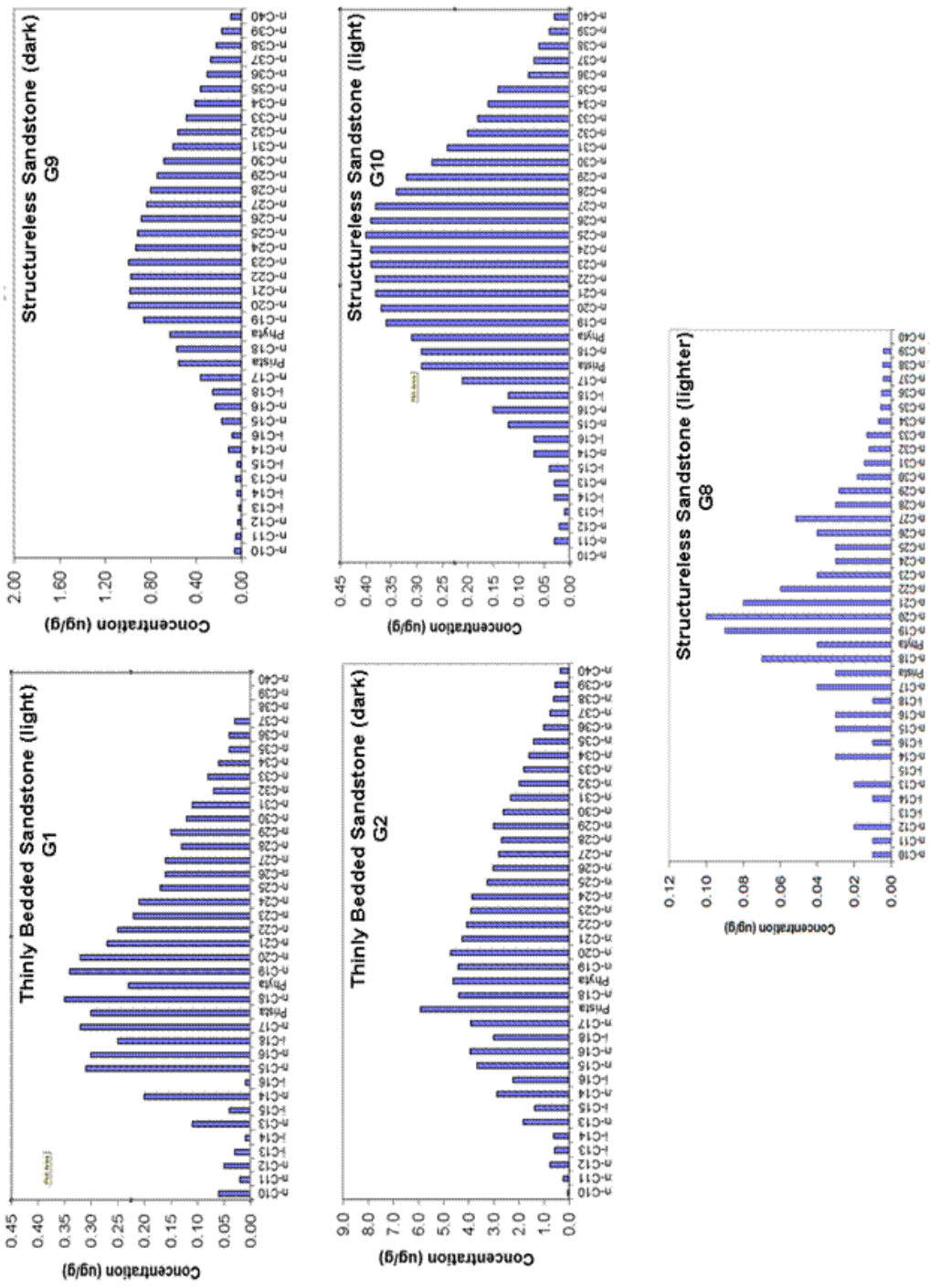

Figure 2. Chain-length distributions of *n*-alkanes and isoprenoid hydrocarbons (pristane and phytane) in sandstones and siltstones from the upper Brushy Canyon Formation.

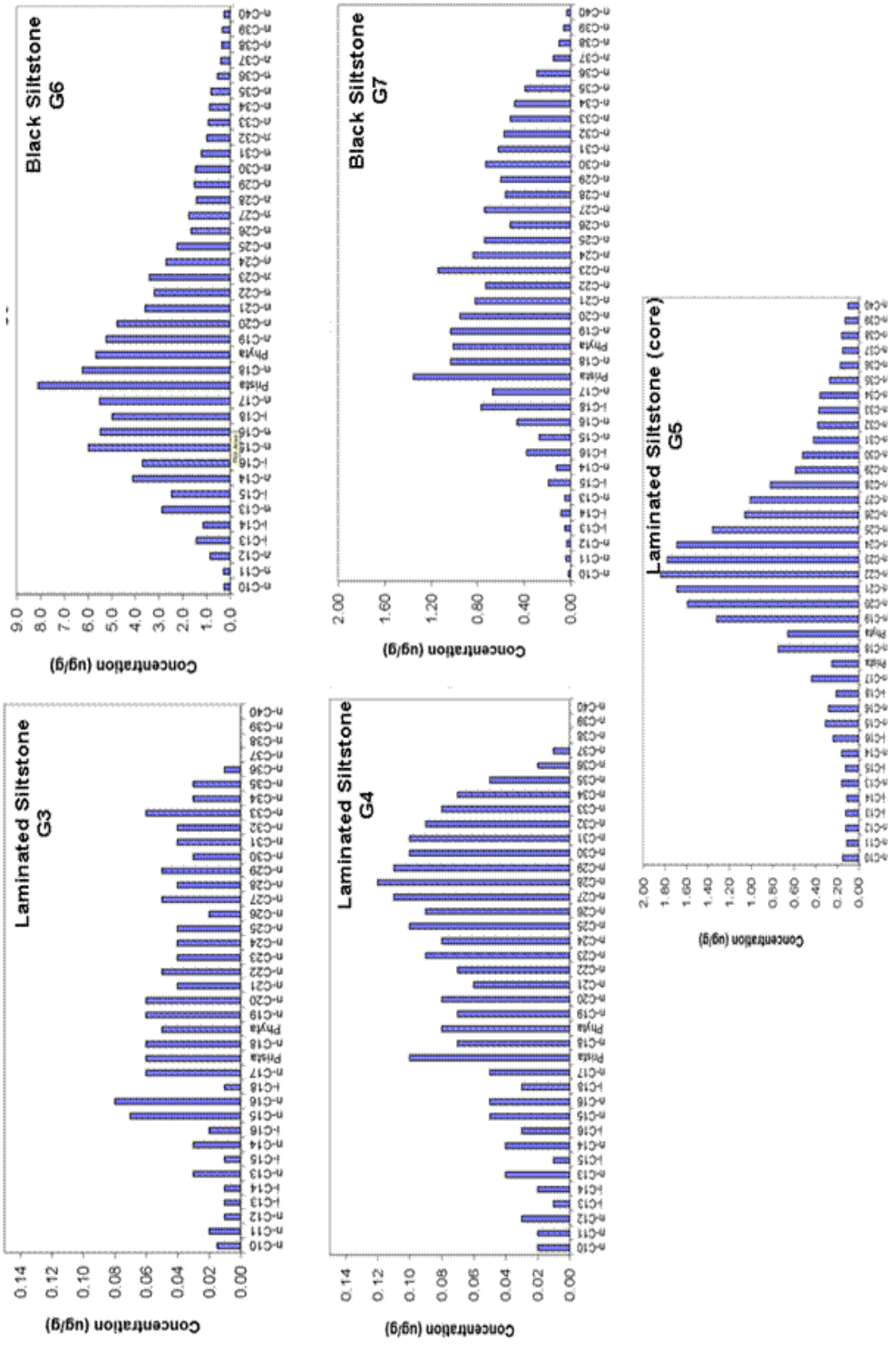

Figure 2. Continued.

The C_{35}-homohopane index or "homohopane index" is the ratio of C_{35}/ (C_{31}-C_{35}) homohopanes, which is generally expressed as a percentage. This ratio in the studied sediments is variable between 7% and 20%. The chromatograms for the all samples (except thinly bedded sandstones: G1 and G2 and core sample: G5) show elevated C_{35} homohopanes (22S+22R doublet) compared to the C_{34} homologs (Figure 3). Thinly bedded sandstones and core sample show regular stair-step progression from C_{31} to C_{35}. The ratios of 22S to 22R isomers of C_{32} hopane (22S/ (22S+22R)) display very little variation and lie between 0.54 and 0.60.

Steranes

Steranes were identified in the all rock samples including C_{29} (20S/ (20S+20R)) steranes and tri-aromatic sterane ratios (TAI/ (TAI+TAII) by mass chromatograms m/z 217 and m/z 231, respectively. C_{29} (20S/ (20S+20R) sterane values were found to be between 0.44-0.52 for all analyzed samples (Table 4). The tri-aromatic steranes were calculated using the ratio of short chain tri-aromatic steranes (TAI: C_{20}+C_{21}) and the sum of short chain and long chain tri-aromatic steranes ((TAI: C_{20}+C_{21}) + (TAII: C_{26}+C_{27}+C_{28})). This ratio ranged between 0.11-0.63 in the all analyzed samples of sandstones and siltstones from the Brushy Canyon Formation (Figure 4, Table 4).

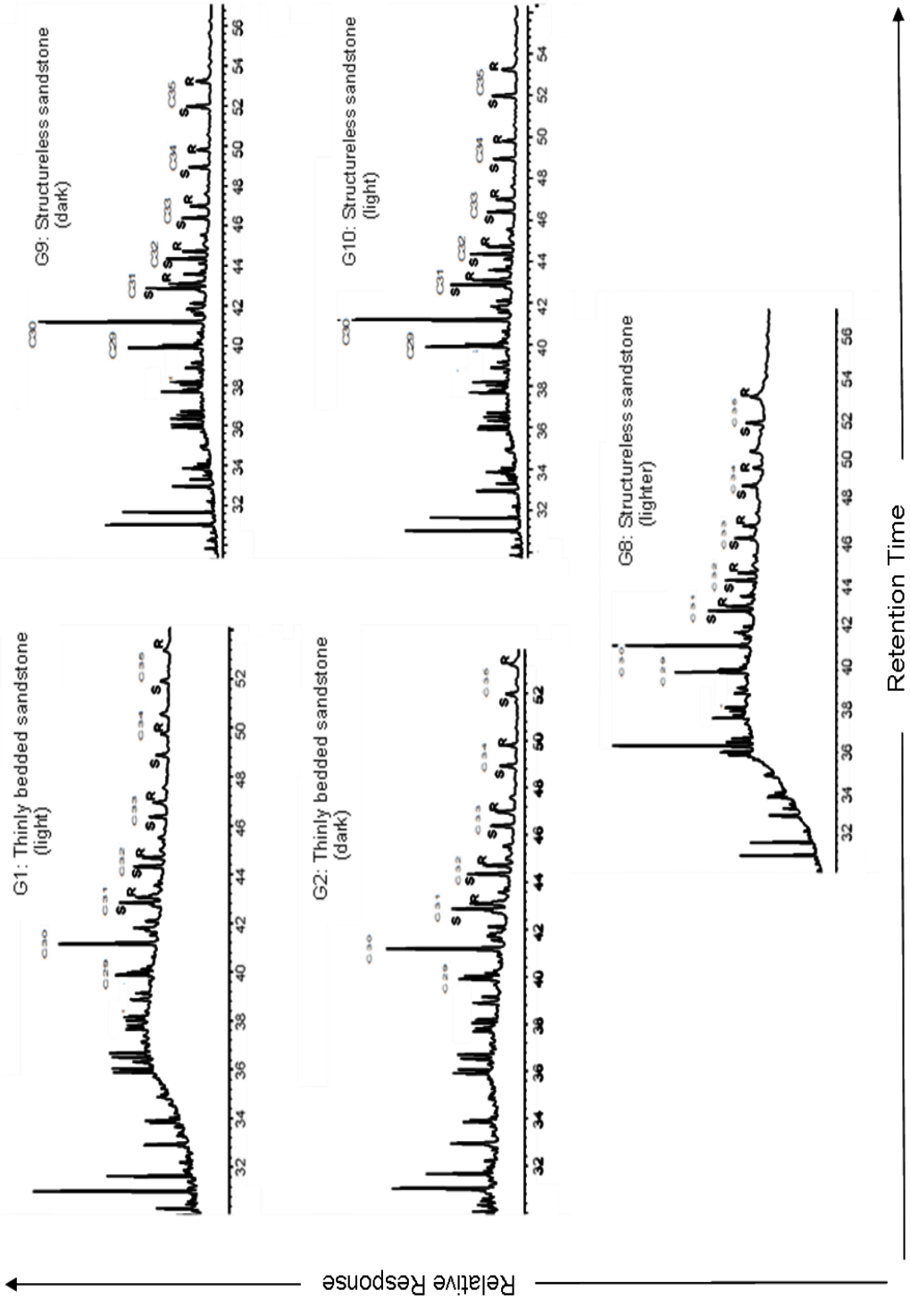

Figure 3. Mass chromatograms (m/z 191) showing the distribution of hopanes in the sedimentary rocks from the upper Brushy Canyon Formation.

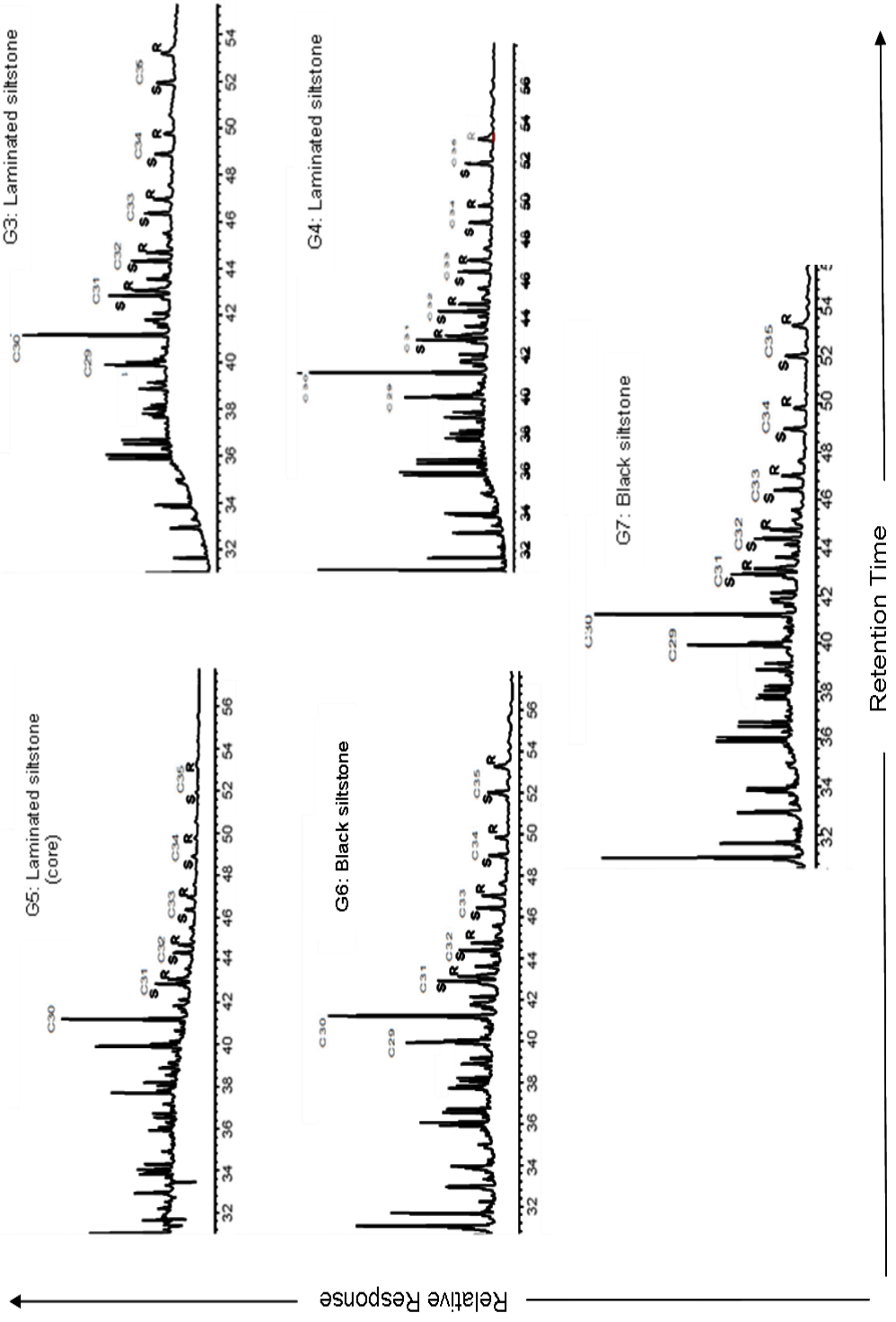

Figure 3. Continued.

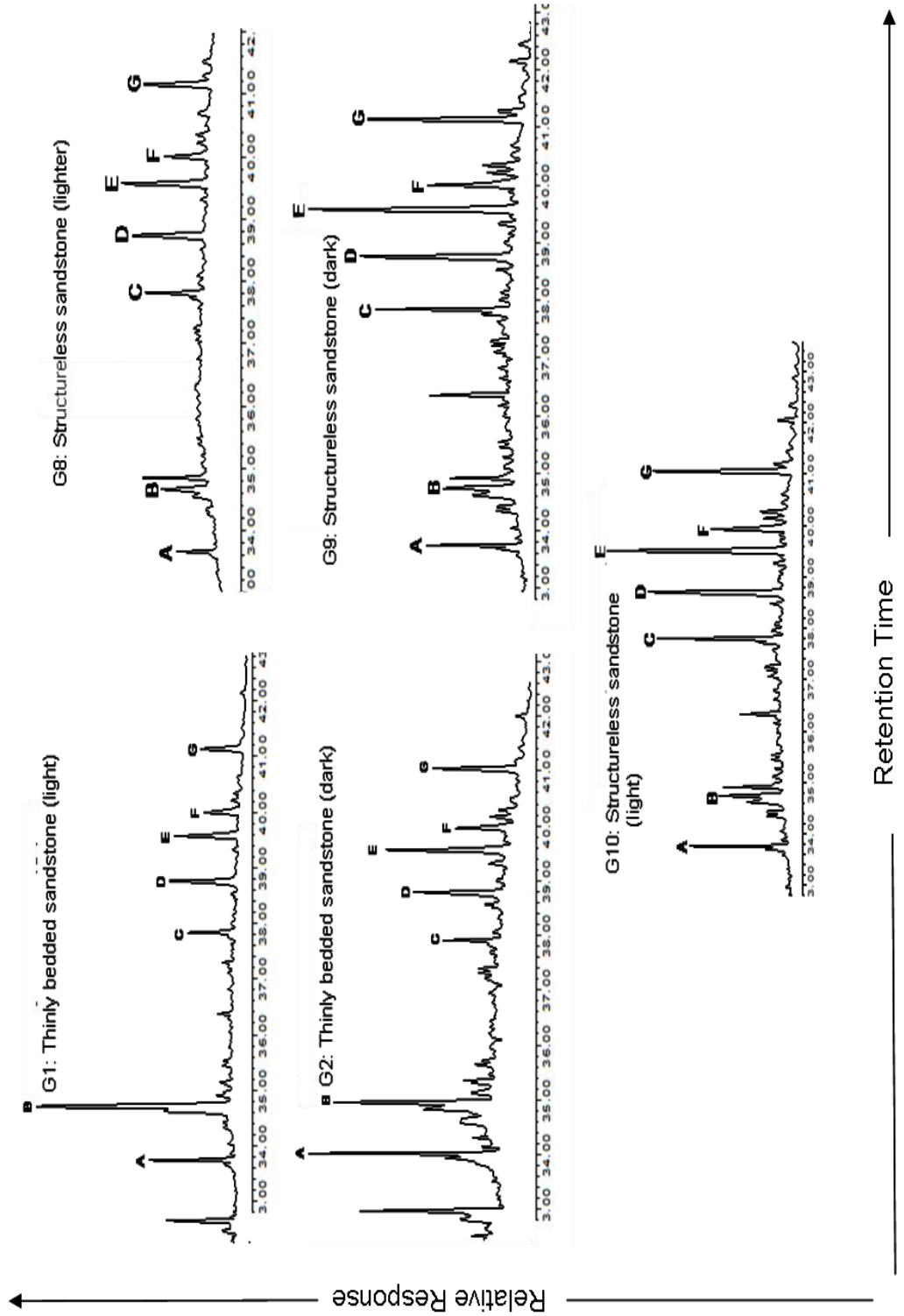

Figure 4. Mass chromatograms (m/z 231) showing the distribution of tri-aromatic steranes in sandstones and siltstones from the upper Brushy Canyon Formation.

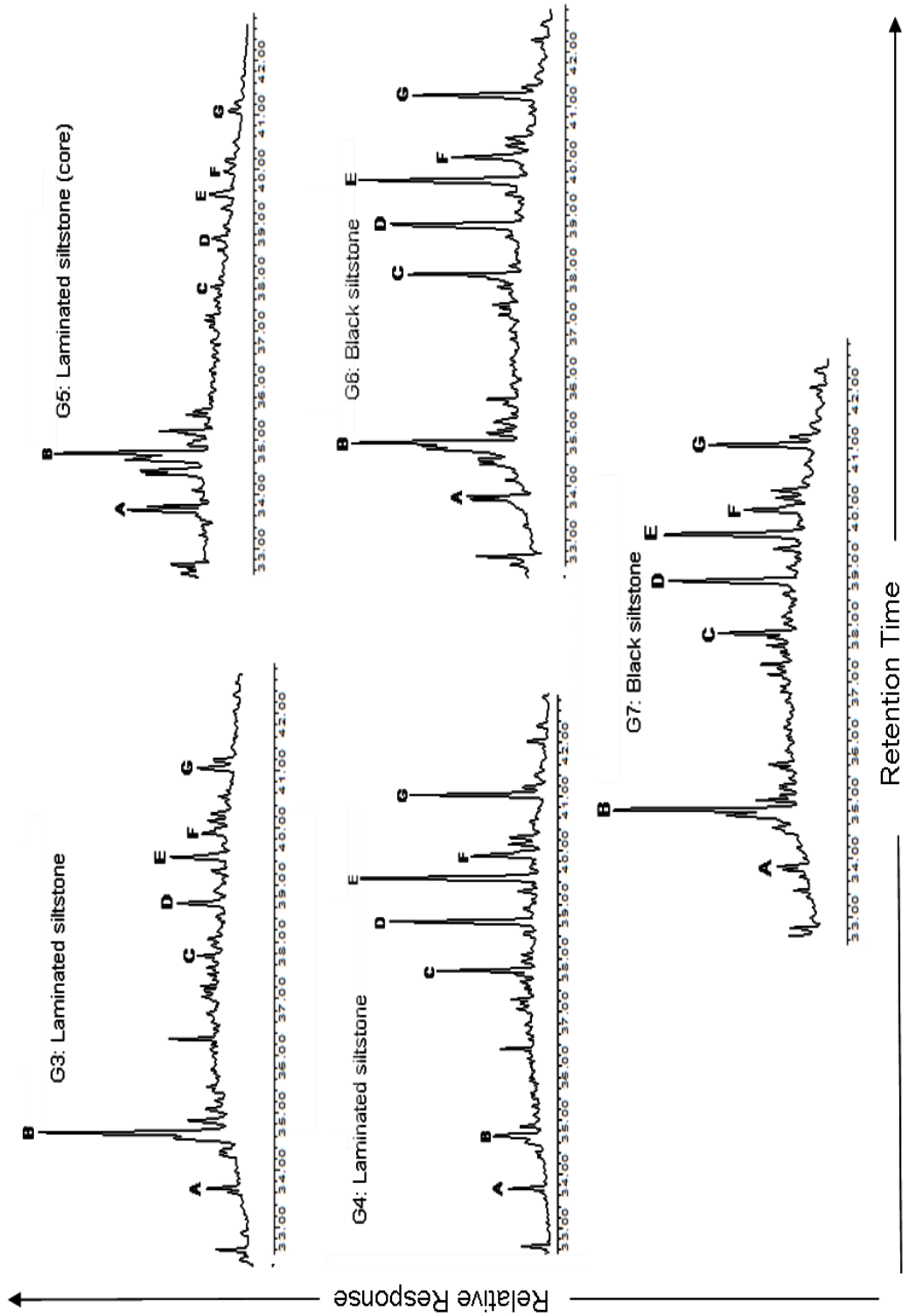

Figure 4. Continued.

Table 3. GC-MS peak identification for Figures 3 and 4.

Peak label	Compound
Hopanes (m/z 191)	
C_{29}	17α (H), 21β (H)- nor-hopane
C_{30}	17α (H), 21β (H)- hopane
C_{31} S	17α (H), 21β (H)- homohopane (22S)
C_{31} R	17α (H), 21β (H)- homohopane (22R)
C_{32} S	17α (H), 21β (H)- bishomohopane (22R)
C_{32} R	17α (H), 21β (H)- bishomohopane (22R)
C_{33} S	17α (H), 21β (H)- trishomohopane (22R)
C_{33} R	17α (H), 21β (H)- trishomohopane (22R)
C_{34} S	17α (H), 21β (H)- tetrakishomohopane (22R)
C_{34} R	17α (H), 21β (H)- tetrakishomohopane (22R)
C_{35} S	17α (H), 21β (H)- pentakishomohopane (22R)
C_{35} R	17α (H), 21β (H)- pentakishomohopane (22R)
Triaromatic steranes (m/z 231)	
A	C_{20}-triaromatic sterane
B	C_{21}-triaromatic sterane
C	C_{26}-triaromatic sterane (20S)
D	C_{26} (20R) + C27 (20S)-triaromatic sterane
E	C_{28}-triaromatic sterane (20S)
F	C_{27}-triaromatic sterane (20R)
G	C_{28}-triaromatic sterane (20R)

DISCUSSION

Thermal Maturity

The carbon preference index (CPI) value, the ratio of odd versus even carbon number n-alkanes, approaches 1.0 with increasing maturity (Peters and Moldowan,

1993). The CPI values for the rock samples from the upper Brushy Canyon Formation, ranging 1.00-1.38, suggest that they are all thermally mature. The C_{32} 22S/ (22S+22R) ratios in the range of 0.55 to 0.62 indicates that the main phase of oil generation has been reached (Seifert and Moldowan, 1986) (Table 4). The values found in this study showed little variation, and they were between 0.54 and 0.60, indicating relatively mature rock extracts. In addition to these parameters, the C_{29} 20S/ (20S+20R) sterane ratio rises with increasing maturity from 0 to about 0.55 (Seifert and Moldowan, 1986). This ratio was found to be between 0.42 and 0.53 for all analyzed extracts, suggesting moderate thermal maturity (Table 4).

Table 4. Data of aromatic hydrocarbons as indicators of maturity in the upper slope of the Brushy Canyon Formation.

Sample ID		**22S/22S+22R C32 hopane**	**20S/20S+20R C29 Sterane**	**TAI/ (TAI+TAII)**
Thinly bedded sandstone (Light)	G1	0.60	0.53	0.50
Thinly bedded sandstone (Dark)	G2	0.59	0.49	0.40
Laminated siltsone (Grey)	G3	0.58	0.52	0.40
Laminated siltstone (Grey)	G4	0.57	0.42	0.11
Laminated siltstone (Core)	G5	0.55	0.47	0.63
Laminated siltstone (Black silt)	G6	0.54	0.42	0.23
Laminated siltstone (Black silt)	G7	0.57	0.46	0.25
Structureless Sandstone (Lighter)	G8	0.58	0.44	0.17
Structureless Sandstone (Dark)	G9	0.59	0.52	0.13
Structureless Sandstone (Light)	G10	0.56	0.46	0.14

The tri-aromatic sterane ratio (TAI/TAI+TAII) is also used to assess thermal maturity and is considered to be independent of the source of organic matter input (Peters and Moldowan, 1993). Where the ratio is 0.1 at the end of the immature stage, it

increases with increasing maturity up to 1.0 at the end of the oil window (Peters and Moldowan, 1993). The TAI/TAI+TAII ratios of all samples fall within a narrow range (0.11 and 0.63) suggesting a similar maturity stage (Table 4). According to these four different maturity parameters, all analyzed samples are thermally mature. Moreover, this indicates that the analyzed extracts from the Brushy Canyon Formation are not modern contaminants.

Organic Matter Source

The distribution of *n*-alkanes in rock extracts and oils has been widely used as a proxy to interpret the source of organic matter (Volkman et al., 1981; Schubert and Stein, 1996). In this study, *n*-alkane distribution patterns and isoprenoid/*n*-alkane (Pr/*n*-C_{17} and Ph/*n*-C_{18}) ratios were examined to address the origin of organic matter in the sedimentary rocks from the Brushy Canyon Formation. Although the gas chromatograms of saturated hydrocarbons showed some dissimilarity in the shape of *n*-alkane distribution in analyzed samples, the *n*-alkane distributions were not entirely distinctive to infer the organic matter source.

The presence of short and long chain n-alkanes, suggesting both marine and terrestrial organic matter input to the basin, were observed in most of the samples. Short chain *n*-alkanes are known to be derived from marine sources with no distinct odd-over-even predominance (Cranwell et al., 1982; Han et al., 1968; Peters and Moldowan, 1993) while mid-chain n-alkanes with a slight odd over even predominance are mainly

from submerged aquatic macrophytes (Ficken at al., 2000). The *n*-alkane distribution patterns in some turbiditic sandstones and ramp siltstones display high relative concentration of short and/or mid chain *n*-alkanes (C_{10}-C_{24}) with low odd-over-even predominance, suggesting marine organic matter input. Terrestrial organic matter input has been characterized by abundance of long chain *n*-alkanes (C_{25}-C_{33}) (Simoneit 1977; Prahl et al., 1980). There are remarkable abundances of long chain *n*-alkanes in the samples of laminated siltstones indicating a significant contribution of land derived organic matter into marine sediments. In addition, relatively higher CPI values in some samples of laminated siltstones also suggest terrestrial organic matter contribution to marine sediments. The presence of odd long chain *n*-alkanes dominated by C_{27}, C_{29} and C_{31} is usually used to infer a higher plant input to the sediment (Eglinton and Hamilton, 1967; Simoneit, 1977).

The isoprenoid/*n*-alkane ratios (Pr/*n*-C17 and Ph/*n*-C18) have been also used to indicate source of organic matter (Lijmbach, 1975; Shanmugam, 1985; Peters et al., 1999). As it is shown in Figure 5, a plot of Pr/*n*-C17 versus Ph/*n*-C18 displays some differences in sources. Most of the samples seem to be derived from mix of terrestrial and marine sources, consisting with previous works which reported presence of algal inputs and terrestrial contributions to the basin based on their hydrogen index data (Hays and Tieh, 1992; Sageman et al., 1998). However, organic matter source variance was ~10-fold greater in ramp siltstones with $P<0.01$ compared to the turbiditic sandstones. This kind of distinct source variation is difficult to envision in turbidity currents because of the primary function of the turbulence, which is to mix and homogenize suspended

material during transport. For this reason, we suggest that siltstones were delivered to the Delaware basin by an alternative transport mechanism which is attributed to Fisher and Sarnthein's (1988) "aeolo-marine" hypothesis.

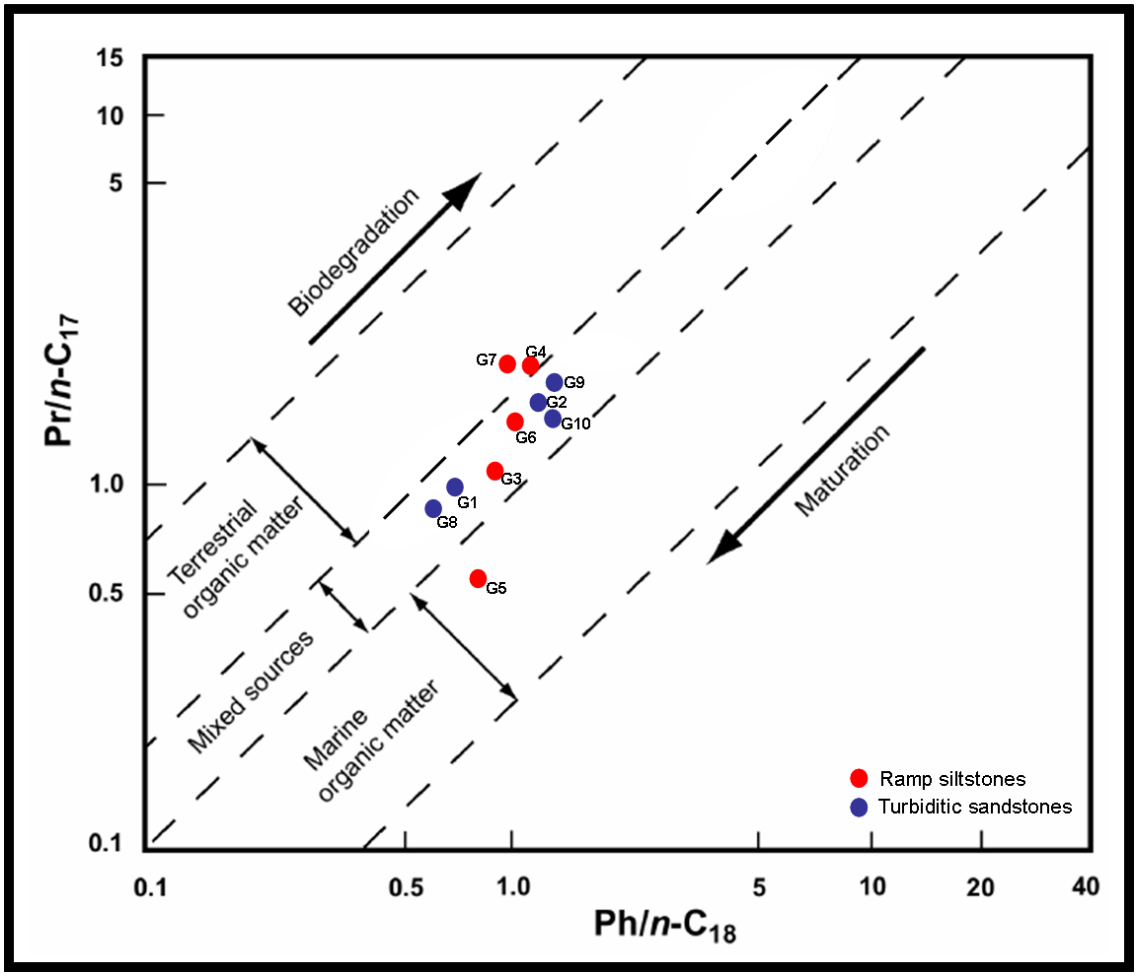

Figure 5. Classification of the sedimentary rocks from the upper Brushy Canyon Formation based on a plot of Pr/*n*-C17 versus Ph/*n*-C18. (Modified after Shanmugam, 1985).

Depositional Environment

The relative distribution of C_{31}-C_{35} 17α(H), 21ß(H) 22S and 22R homohopanes in marine sediments and petroleum have been used as indicators of redox potential (Eh) during and after deposition processes (Peters and Moldowan, 1991; Peters et al., 2005). High C_{35}-homohopane indices typically indicate highly reducing (low Eh) marine depositional environments (Peters and Moldowan, 1991). Pentacyclic triterpenoids, including precurcors of the hopanes, are found in prokaryotic microorganisms and higher plants, but appear to be absent in algae (Peters and Moldowan, 1991). Bacteria are known as a major source for hopanoids in sedimentary rocks. The extended hopanes or "homohopanes" (C_{31}-C_{35}) are related to specific bacteriohopanepolylols in bacteria, such as bacteriohopanetetrol (Peters et al., 2005). Hopanes are originated from precurcors in bacterial membranes (Ourisson et al., 1979). The hopanoids undergo net reduction to hopanes during diagenesis.

The terpane mass chromatograms in Figure 3 (m/z 191) for the ramp sediments of the upper Brushy Canyon Formation display two different homohopane distributions in terms of the C_{35} homohopanes (22S+22R doublet) compared to the C_{34} homologs. The structureless sandstone (G8, G9, and G10) and laminated siltstone (G3 and G4) outcrop samples showing high concentrations of C_{35} homohopanes seem to be deposited under anoxic conditions. In contrast, the regular stair-step progression from C_{31} to C_{35} homohopanes in thinly bedded sandstones (G1 and G2) and core sample (G5) suggest that anoxic conditions did not occur during the time of deposition (Peters and

Moldowan, 1991). However, suboxic or dysoxic conditions may have existed (Tyson and Pearson, 1991). The existence of anoxic conditions in the water column is consistent with early studies in the Delaware basin (King, 1948; Harms, 1974). The characterization of dysoxia in some of the samples is not consistent with stable anoxia; however it is more consistent with more recent interpretations of hydrogen index data and pyritization records in related sedimentary rocks from the Brushy Canyon Formation (Sageman et al., 1998).

CONCLUSIONS

Terrestrial organic content was quantified in sandstones and siltstones of the Middle Permian Brushy Canyon Formation using a crossplot of pristane/*n*-C_{17} versus phytane/*n*-C_{18}. Ramp siltstones showed ~10-fold greater variation in terrestrial organic matter content than did turbiditic sandstones. This observation is more consistent with the "aeolo-marine" interpretation of ramp siltstones (Fisher and Sarnthein, 1988), and suggests that terrestrial organic matter was delivered to the Delaware Basin by wind transport during deposition of the Brushy Canyon Formation.

The relatively higher terrestrial organic matter input in organic-rich, black siltstones, which were proven as economic oil source rocks (Hays and Tieh, 1992), suggests that geochemical cycle in the basin could have been affected by delivery of windblown dust. It is also pointed out that the moderate thermal maturation, which is observed in all samples, indicates that they are not modern contaminants.

Quantification of organic biological markers, including biomarker parameters and *n*-alkane distributions, in sedimentary rock extracts may address problems of understanding the process of sediment and organic matter delivery in ancient, deep-water sedimentary environments. Hence, differences in organic matter source variance may also be significant for understanding the probable windblown dust delivery of terrestrial organic matter to a basin.

CHAPTER III

SUMMARY AND CONCLUSIONS

Organic contents of sandstones and siltstones of the Middle Permian Brushy Canyon Formation were compared in order to test hypotheses regarding the origin of the two types of host rocks in the study area. The biomarker parameters and *n*-alkane distributions allowed us to recognize different organic matter inputs, assess the oxicity of their depositional environment and also determine their degree of maturity. The results indicate that these two types of host rocks were delivered to the Delaware Basin by different transport mechanisms during deposition of the Brushy Canyon Formation and yield the following conclusions:

1- The variation of terrestrial organic matter content in ramp siltstones was much (~10-fold) greater in comparison to turbiditic sandstones, suggesting windblown dust transport. The difference in source variance is more consistent with Fischer and Sarnthein's (1988) "aeolo-marine" hypothesis for siltstones, which form the bulk of the Brushy Canyon Formation ramp deposits.

2- Although anoxic depositional environment was observed in most of the samples; it was not stable in the whole basin. The presence of dysoxic conditions was observed in some samples from different locations of the basin, suggesting that water chemistry could have been different even though they have the same source.

3- The biomarker maturity parameters indicate moderate thermal maturity level for all samples of sandstones and siltstones, suggesting that they are not modern contaminants.

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